

Supporting Information

Facile Synthesis of N-rich Porous Azo-linked Framework for Selective CO₂ Capture and Conversion

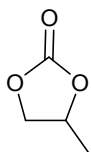
Jinquan Wang and Yugen Zhang*

*Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos, Singapore 138669
(Singapore), Email: yqzhang@ibn.a-star.edu.sg.*

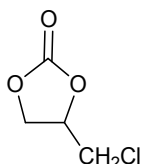
Supporting information

1. Characterization of cyclic carbonates in Table 2	S2
2. Supporting Tables	S4
3. Supporting Figures	S5
4. Cartesian coordinates for the optimized geometries in Figure S11	S11

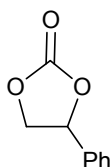
1. Characterization of cyclic carbonates



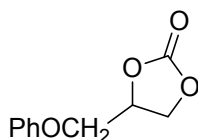
^1H NMR (CDCl_3 , TMS, 400 MHz): δ 4.86-4.94 (m, 1H), 4.60 (t, $J=8.0$ Hz, 1H), 4.05 (t, $J=8.8$ Hz, 1H), 1.49 (d, $J=6.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , TMS, 100.4 MHz): δ 154.95 (C=O), 73.51, 70.46, 18.95.



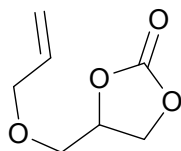
^1H NMR (CDCl_3 , TMS, 400 MHz): δ 4.98 (m, 1H), 4.58 (t, 1H, $J=8.4$ Hz), 4.39 (dd, 1H, $J=6.0$ Hz), 3.80 (dd, 1H, $J=5.2$ Hz), 3.71 (dd, 1H, $J=3.2$ Hz); ^{13}C NMR (CDCl_3 , TMS, 100.4 MHz): δ 154.95 (C=O), 73.51, 70.46, 43.83.



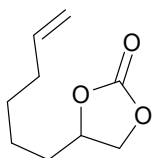
^1H NMR (CDCl_3 , TMS, 400 MHz): δ 7.35-7.44 (m, 5H), 5.68 (t, 1H, $J=8.0$ Hz), 4.80 (t, 1H, $J=8.4$ Hz), 4.34 (t, 1H, $J=8.4$ Hz); ^{13}C NMR (CDCl_3 , TMS, 100.4 MHz): δ 154.81 (C=O), 135.70, 129.63, 129.12, 125.81, 77.92, 71.10.



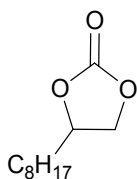
^1H NMR (CDCl_3 , 400 MHz): δ 7.31 (t, $^3J=8.0$ Hz, 2H), 7.02 (t, $^3J=7.4$ Hz, 1H), 6.91 [d, $^3J=8.0$ Hz, 2H], 5.03 [m, 1H], 4.62 [t, $^3J=8.4$ Hz, 1H], 4.55 (dd, $^3J=8.4$ Hz), 4.24 (dd, $^3J=3.6$ Hz, 1H), 4.15 (dd, $^3J=4.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , TMS, 100.4 MHz): δ 157.71, 154.65, 129.62, 121.92, 114.57, 74.11, 68.84, 66.17.



^1H NMR (CDCl_3 , 400 MHz): δ 5.8-6.0 (t, 1H), 5.0-5.2 (d, 2H), 4.4-4.7 (3H), 4.0-4.1 (m, 2H), 3.5-3.8 (d, 2H). ^{13}C NMR (CDCl_3 , TMS, 100.4 MHz): δ 155.90, 133.88, 117.47, 72.05, 72.30, 68.92, 66.24.



^1H NMR (CDCl_3 , TMS, 400 MHz): δ 5.8–6.0 (t, 1H), 5.0–5.2 (d, 2H), 4.7 (m, 1H), 4.5 (dd, 1H), 4.04 (dd, 1H, $J=8.4$ Hz), 2.4–2.7 (m, 2H), 2.1 (m, 2H), 1.43–1.55 (m, 4H); ^{13}C NMR (CDCl_3 , TMS, 100.4 MHz): δ 155.2 (C=O), 139.2, 115.6, 70.4, 66.3, 36.5, 33.8, 29.6, 25.3.



^1H NMR (CDCl_3 , TMS, 400 MHz): δ 4.6–4.8 (m, 1H), 4.50 (dd, 1H, $J=8.4$ Hz), 4.04 (dd, 1H, $J=8.4$ Hz), 1.6–1.9 (m, 2H), 1.1–1.6 (m, 12H), 0.86 (t, 2H); ^{13}C NMR (CDCl_3 , TMS, 100.4 MHz): δ 155.2 (C=O), 77.1, 69.5, 34.0, 31.9, 29.4, 29.2, 29.2, 24.5, 22.7, 14.2.

2. Supporting Tables

Table S1 Porosity analysis of PAF synthesized in different solvent.^a

<i>Solvent</i>	S_{BET} (m ² /g)	S_{micro} (m ² /g)	V_{total} (cm ³ /g)	V_{micro} (cm ³ /g)
1,2-Dichloroethane	146	67	0.13	0.03
CH ₃ CN	20	-	0.026	-
Dioxane	31	23	0.016	0.011
Toluene	0	0	0	0
DMF	309	238	0.15	0.11
DMSO	702	493	0.35	0.23

^a3, 3'-diaminobenzidine (1 mmol), (diacetoxyiodo) benzene (4 mmol) and solvent (10 mL), RT, 24 h.

Table S2 Porosity and CO₂ capture analysis of PAF synthesized in time.^a

<i>Time</i>	S_{BET} (m ² /g)	S_{micro} (m ² /g)	V_{total} (cm ³ /g)	V_{micro} (cm ³ /g)	CO ₂ uptake (wt%/mmol) at 273 K
40 min	725	560	0.37	0.26	15.3/3.48
24 h	742	523	0.40	0.24	18.2/4.16
168 h ^a	654	513	0.33	0.24	16.5/3.76

^a3, 3'-diaminobenzidine (1 mmol), (diacetoxyiodo) benzene (4 mmol) and DMSO (10 mL), RT.

3. Supporting Figures



Fig. S1 As synthesized PAF material. Synthesis condition: 3, 3'-diaminobenzidine (1 mmol), (diacetoxyiodo) benzene (4 mmol) and DMSO (10 mL), RT, 24 h.

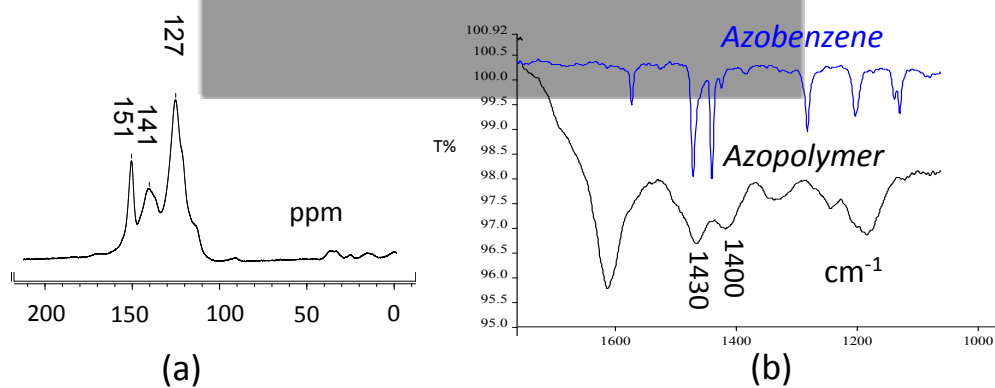


Fig. S2 (a) Solid ^{13}C NMR spectrum of PAF, (b) FI-IR spectra for azopolymer (PAF) and azobenzene

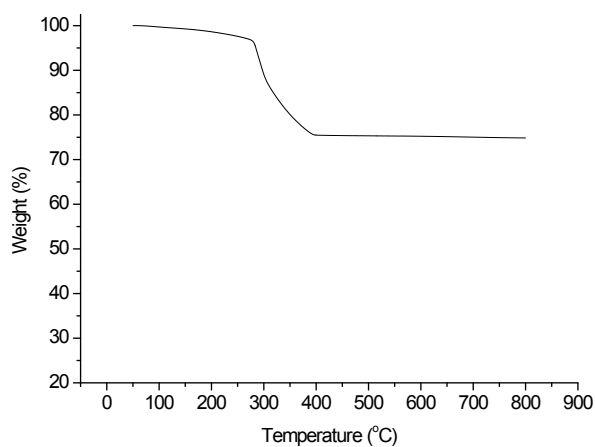


Fig. S3 TGA curve of PAF

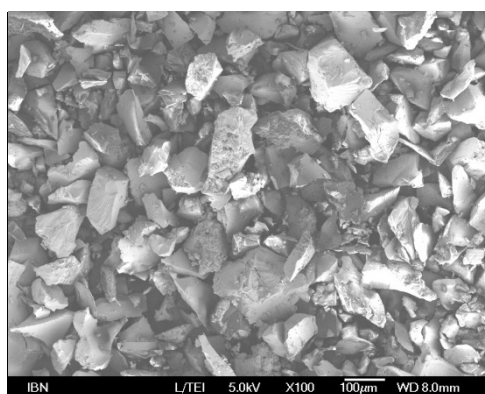


Fig. S4 SEM image of PAF

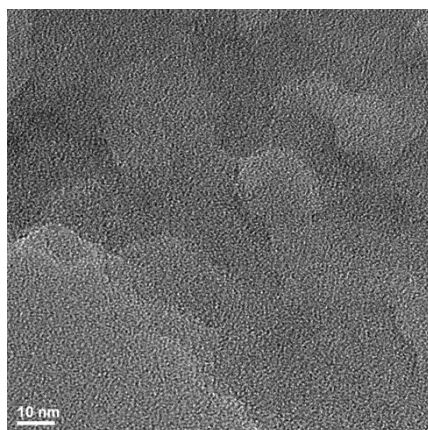


Fig. S5 TEM image of PAF

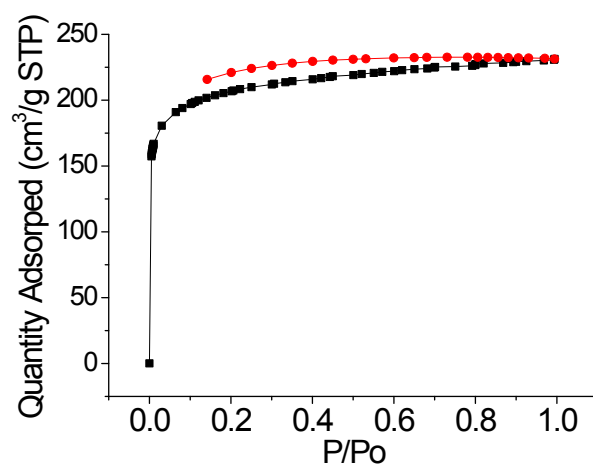


Fig. S6 N₂ adsorption-desorption isotherms of PAF

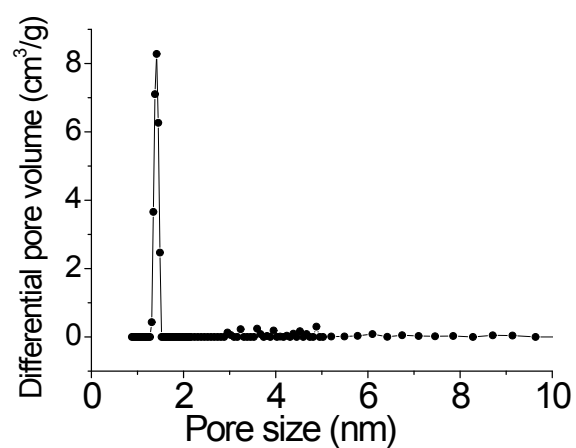


Fig. S7 Pore size distributions of PAF

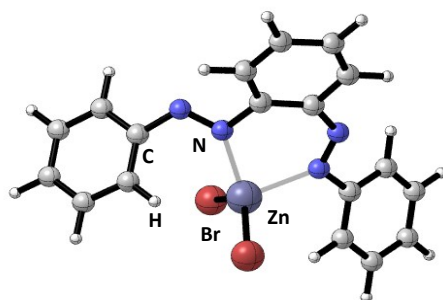


Fig. S8 The optimized structure between ZnBr_2 and the simulated complex with two azo groups

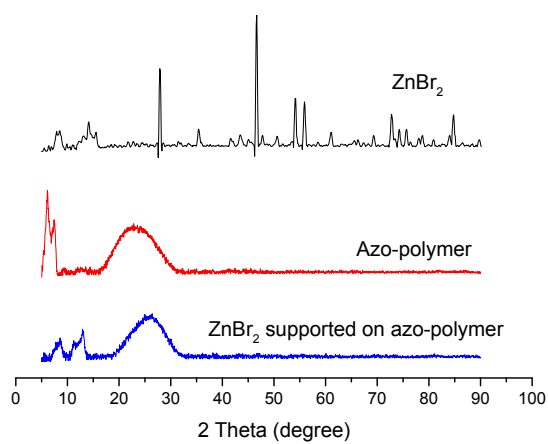


Fig. S9 XRD patterns of ZnBr_2 , porous azo-linked framework material (PAF) and PAF supported ZnBr_2 material.

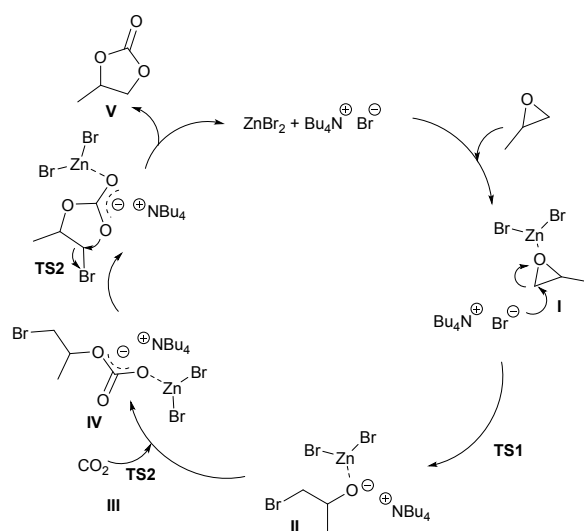


Fig. S10 Mechanistic hypothesis of the catalytic cycle.

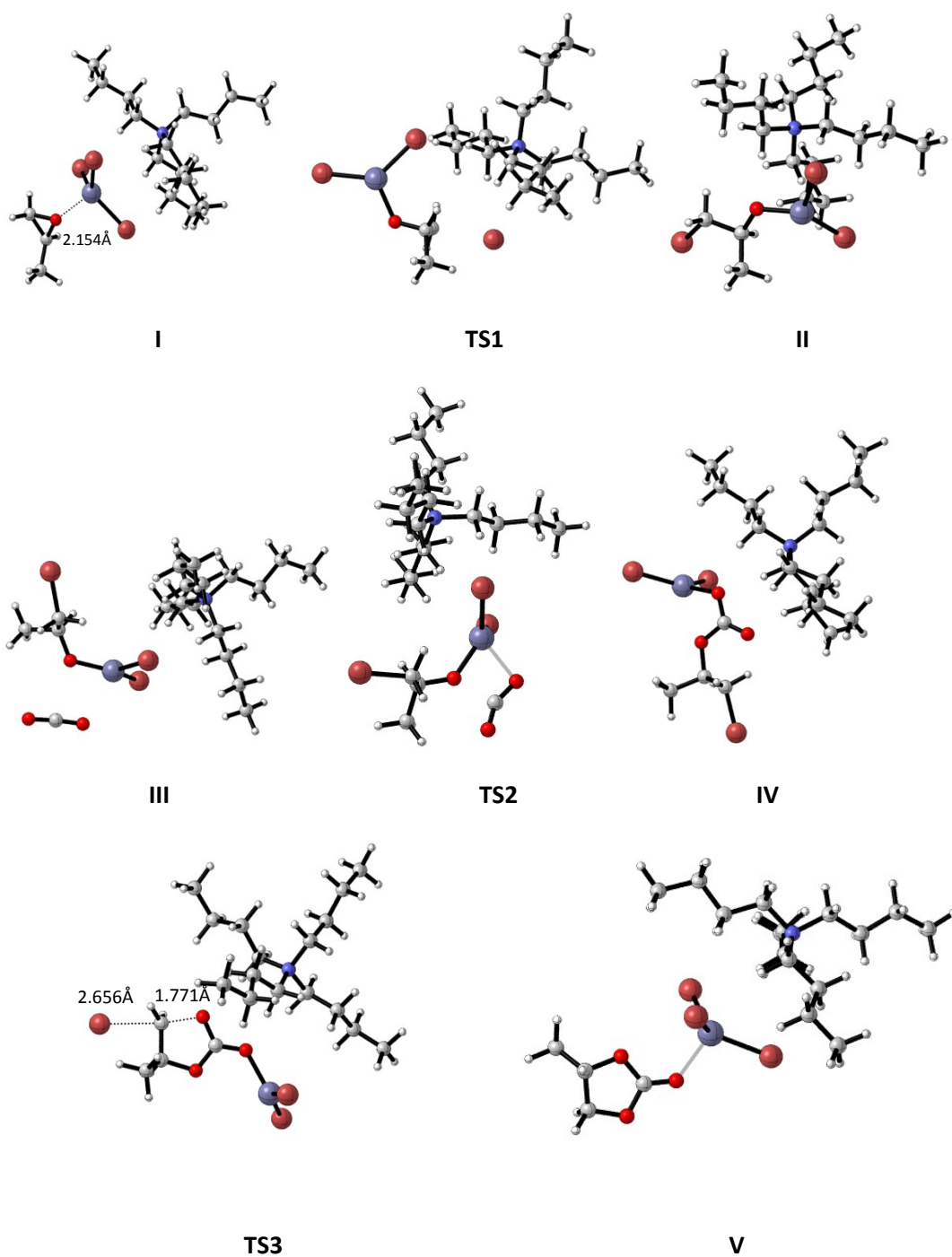


Fig. S11 Optimized geometries for the intermediates and transition states. H: white, C: gray, N: blue, O: red, Br: brown, Zn: light blue. Bond lengths and distances are in Å.

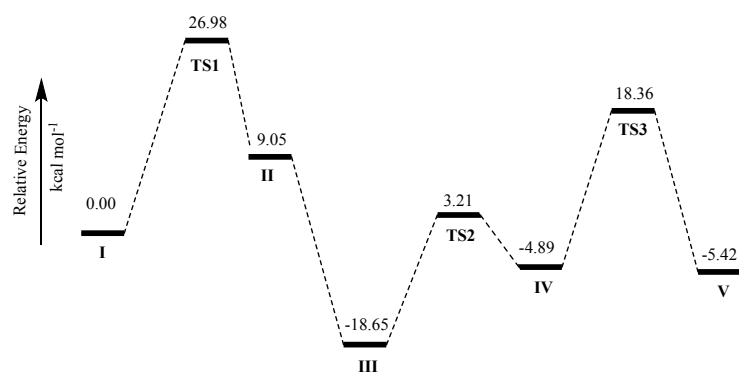


Fig. S12 Relative energies for fixation of CO₂ with PO catalyzed by ZnBr₂ and TBAB, relative energies at the B3PW91/6-311++G (d, p) level.

4. Cartesian coordinates for the optimized geometries in Figure S11

I

C	5.16911500	0.79019400	0.07737000
C	5.01051800	-0.36467400	0.96927800
H	6.02649600	0.84165200	-0.58641100
H	4.68605200	1.72811700	0.33053300
H	4.38432700	-0.21489100	1.84504600
Br	1.78118300	1.81456400	1.18614000
O	4.24599000	-0.27582400	-0.27009700
C	5.99734400	-1.49372500	1.03690600
H	6.69879300	-1.32449000	1.85963900
H	5.47873300	-2.43788000	1.21877300
H	6.56130700	-1.57777200	0.10577400
C	-3.89177800	0.88688300	-0.12480300
C	-4.92350500	-0.23871600	-0.19685700
H	-4.09499400	1.58527100	-0.93911600
H	-3.99783300	1.43989000	0.80881700
C	-6.33840500	0.33967200	-0.03127400
H	-4.86122200	-0.74725600	-1.16237000
H	-4.75317800	-0.99108100	0.57335900
C	-7.42786200	-0.73037400	-0.14228300
H	-6.41582000	0.84058700	0.94080400
H	-6.50881400	1.11334700	-0.78942300
H	-8.42136900	-0.29303300	-0.01766600
H	-7.40182000	-1.22314700	-1.11867100
H	-7.30599000	-1.50203100	0.62353100
C	-2.14031300	-0.47436100	-1.36969700
C	-2.23065900	-1.96458500	-1.05375000
H	-1.12563600	-0.26019000	-1.71030000
H	-2.82181900	-0.19922400	-2.17836700

C	-1.92017100	-2.76942200	-2.32823700
H	-1.48787700	-2.22887600	-0.29735500
H	-3.21498200	-2.25189000	-0.67856800
C	-1.93165900	-4.27915700	-2.07518200
H	-2.64980700	-2.51999400	-3.10899300
H	-0.93889500	-2.46950900	-2.70863300
H	-1.71382100	-4.83059200	-2.99326900
H	-1.17684500	-4.55490400	-1.33401200
H	-2.90646600	-4.61644000	-1.70742600
C	-1.75988800	0.13477400	1.07888000
C	-2.54119900	-0.76379800	2.03382400
H	-1.51972100	1.06404900	1.59049600
H	-0.81265800	-0.33212700	0.81060600
C	-1.69372900	-1.02622800	3.29103500
H	-3.48157500	-0.29018200	2.33583400
H	-2.78995700	-1.72020900	1.57071800
C	-2.41118300	-1.92654500	4.29985100
H	-0.74453000	-1.48142100	2.99332200
H	-1.44100000	-0.07066800	3.76439100
H	-1.78940900	-2.09531100	5.18241200
H	-3.35340700	-1.48221600	4.63773100
H	-2.63967500	-2.90489100	3.86592400
C	-1.68643600	1.82714600	-0.72777900
C	-1.93855900	3.11551400	0.04954800
H	-1.98712600	1.95099600	-1.77000100
H	-0.62427100	1.58541400	-0.71546800
C	-1.09863100	4.25335800	-0.55755400
H	-2.99482500	3.40084800	0.02435000
H	-1.65355200	3.00297100	1.09907200
C	-1.29717900	5.57968400	0.17994800

H	-0.04316100	3.96838300	-0.52707800
H	-1.36245600	4.37704100	-1.61448700
H	-0.69415300	6.37059900	-0.27269200
H	-2.34313500	5.90279600	0.15374600
H	-0.99725900	5.49556900	1.22859400
Zn	2.09818200	-0.11075500	-0.29696300
Br	1.47326900	0.29479900	-2.58816600
Br	1.41792300	-2.21573500	0.68851200
N	-2.41258300	0.54730200	-0.24940800

TS1

C	-1.77662000	2.11211800	0.72212500
C	-2.11013800	2.29060500	-0.68419600
H	-2.11396500	2.83360700	1.44813900
H	-1.38119300	1.17108100	1.06140600
H	-1.55655700	1.64618200	-1.36921900
Br	0.71981700	3.02759900	1.11370500
O	-3.28436100	1.65419500	-0.14611100
C	-2.35964600	3.67366300	-1.23066100
H	-1.40692100	4.17898300	-1.40680800
H	-2.90918600	3.61230300	-2.17335400
H	-2.94554300	4.26527100	-0.52426400
C	2.93663500	-2.00960400	0.05327400
C	3.76229500	-2.25843500	-1.20819000
H	2.02299000	-2.60252700	-0.01681700
H	3.47876600	-2.34902500	0.93684900
C	4.15331100	-3.74317900	-1.29134100
H	3.17935000	-1.99779700	-2.09507900

H	4.66737900	-1.65035900	-1.22631100
C	4.95341400	-4.06880800	-2.55555900
H	4.74117400	-4.01538800	-0.40668900
H	3.24880300	-4.36149000	-1.26168100
H	5.22190100	-5.12732400	-2.58774500
H	4.37722800	-3.84509700	-3.45804400
H	5.88039000	-3.48916100	-2.59891700
C	1.91189900	0.12983400	-0.87569900
C	2.87566500	0.86537100	-1.80272900
H	1.22307900	0.87180100	-0.46934900
H	1.33004300	-0.62108400	-1.41259300
C	2.07943400	1.50528200	-2.95326600
H	3.38173000	1.66420000	-1.25444300
H	3.64296600	0.21104700	-2.22130300
C	2.97368100	2.29245500	-3.91470100
H	1.54191000	0.72578300	-3.50556200
H	1.31982400	2.17031200	-2.53053500
H	2.38505900	2.73713900	-4.72077100
H	3.49238200	3.10451800	-3.39667800
H	3.73131500	1.64903500	-4.37342900
C	3.49824900	0.25853400	1.10928800
C	4.96049700	0.19835500	0.67304100
H	3.44191200	-0.05983900	2.14921900
H	3.10344800	1.27581000	1.06526300
C	5.79642400	1.15742600	1.53745500
H	5.35562600	-0.81579400	0.79133600
H	5.08056300	0.47131100	-0.37618000

C	7.28235700	1.13751500	1.16969900
H	5.40374700	2.17422600	1.43124500
H	5.67740100	0.89311200	2.59463600
H	7.85026200	1.82684800	1.79898800
H	7.71243800	0.13944000	1.29882500
H	7.43758500	1.43569700	0.12847600
C	1.24067400	-0.70939500	1.30188200
C	1.37493800	-1.60470100	2.53169100
H	0.42701600	-1.06673500	0.66759900
H	1.02138200	0.32149800	1.59002000
C	0.10389700	-1.49126600	3.39262800
H	1.51145400	-2.65211600	2.24761500
H	2.23677200	-1.32469500	3.14640900
C	0.15513500	-2.38858200	4.63167700
H	-0.03252600	-0.44837600	3.69753000
H	-0.76795500	-1.75562200	2.78480900
H	-0.75789800	-2.28874900	5.22311200
H	0.25729900	-3.44247200	4.35555800
H	0.99939200	-2.12767500	5.27737500
Zn	-3.73733300	-0.24863100	-0.37639500
Br	-1.82533400	-1.47603100	-1.08537000
Br	-5.87345500	-0.95251800	0.14197300
N	2.46792200	-0.59463100	0.36468900

II

C	-3.40272000	1.37663300	0.96469700
C	-2.97430300	0.40259400	-0.13968100

H	-4.06875300	0.90413500	1.68402300
H	-2.53524500	1.78486900	1.47555400
H	-2.48802300	0.98607700	-0.93945600
Br	-4.38616700	2.97309700	0.28360400
O	-2.05847100	-0.46055100	0.49031800
C	-4.16319200	-0.34359100	-0.74666000
H	-4.89591000	0.34538400	-1.17501500
H	-3.81845500	-1.00597600	-1.54521700
H	-4.65463200	-0.94856400	0.02180200
C	2.31849900	-0.38837800	0.41766700
C	2.92849500	-0.65343900	-0.95665100
H	1.51821400	-1.11029500	0.58126000
H	3.05602300	-0.54663200	1.20562700
C	3.52768000	-2.07053500	-0.98101500
H	2.15415600	-0.59755600	-1.72554100
H	3.70763600	0.06870300	-1.20752900
C	4.08744800	-2.43730300	-2.35776000
H	4.32122600	-2.14604400	-0.22705500
H	2.75614600	-2.79243200	-0.69590600
H	4.51408600	-3.44321800	-2.34909100
H	3.30050000	-2.41712400	-3.11634700
H	4.87594900	-1.74390000	-2.66863100
C	0.85619000	1.50762800	-0.47288100
C	1.54738900	2.26157000	-1.60686300
H	0.11836400	2.16960000	-0.01704200
H	0.31746800	0.64188400	-0.85855100
C	0.50388800	2.65507800	-2.66739200

H	2.02735500	3.17092800	-1.23125900
H	2.32011700	1.65536200	-2.08039000
C	1.11893600	3.44356300	-3.82634000
H	0.02208500	1.74973800	-3.04996400
H	-0.28693900	3.25145100	-2.19821700
H	0.35668300	3.71141300	-4.56165800
H	1.58430000	4.37111600	-3.47780500
H	1.88499200	2.85771300	-4.34326200
C	2.70658400	2.01729200	1.19209400
C	4.08043300	2.08453400	0.52703800
H	2.85069800	1.80893200	2.25167800
H	2.19757400	2.98064600	1.11860300
C	4.91893600	3.20305400	1.16723000
H	4.60613000	1.13390900	0.65177800
H	3.99911400	2.26838800	-0.54464300
C	6.32263300	3.30303000	0.56380700
H	4.40032400	4.16139100	1.04686100
H	4.99693000	3.02981400	2.24701700
H	6.89540700	4.10521500	1.03496700
H	6.88049100	2.37197800	0.70040900
H	6.27948800	3.51149700	-0.50920400
C	0.66554200	0.79717900	1.84764300
C	1.11444800	0.00212700	3.06982000
H	-0.21158500	0.32636100	1.39234500
H	0.38753100	1.81374200	2.13753400
C	0.00324800	0.02548100	4.13441700
H	1.30486700	-1.03851200	2.79916900

H	2.03468300	0.40497800	3.50915000
C	0.37110800	-0.79183700	5.37524900
H	-0.20638100	1.06221300	4.42499900
H	-0.91627600	-0.37005000	3.69247000
H	-0.43124400	-0.75767100	6.11624500
H	0.54060000	-1.84076800	5.11776700
H	1.27994600	-0.40966200	5.85133500
Zn	-1.22048900	-1.94452200	-0.33071900
Br	-0.63732000	-1.76086600	-2.63062800
Br	-0.14651700	-3.46134600	1.13274500
N	1.69563600	0.98457300	0.70478500

III

C	3.94687800	1.40002300	0.38518900
C	3.61838600	0.19886900	1.28129000
H	4.93542600	1.31263800	-0.06176900
H	3.19442200	1.52920600	-0.38802300
H	2.71506300	0.45019100	1.86262100
Br	3.96265400	3.14871500	1.36706600
O	3.39886000	-0.89430800	0.42563000
C	4.74155500	-0.13373200	2.26172400
H	4.96118300	0.70810500	2.92364300
H	4.45266200	-0.99378100	2.86996400
H	5.64900700	-0.39757500	1.71072700
C	-2.78850500	0.08635100	-1.08429800
C	-3.30379300	-1.34660200	-0.97752500
H	-1.75799600	0.05073300	-1.44275600

H	-3.37469100	0.65914700	-1.80435600
C	-3.28749100	-1.99049800	-2.37457100
H	-2.64646100	-1.92768000	-0.32687100
H	-4.31601100	-1.39584300	-0.57160600
C	-3.72987200	-3.45581700	-2.34484200
H	-3.93939600	-1.42219000	-3.04991500
H	-2.27553700	-1.92339600	-2.78681300
H	-3.70840600	-3.88980000	-3.34750400
H	-3.06746800	-4.05096300	-1.71073800
H	-4.74968500	-3.55905800	-1.95995300
C	-2.19149500	0.17647400	1.39656300
C	-3.15445700	-0.64451900	2.25144800
H	-1.73293200	0.93728400	2.03083700
H	-1.39490900	-0.46021900	1.00706000
C	-2.38029600	-1.28658000	3.41690100
H	-3.94703900	-0.01318900	2.66557900
H	-3.63311700	-1.43253100	1.66866300
C	-3.28378800	-2.13097400	4.31919300
H	-1.57373600	-1.90608700	3.01431700
H	-1.90140600	-0.49986400	4.01190900
H	-2.71156800	-2.57267200	5.13826800
H	-4.08626100	-1.53047300	4.75992600
H	-3.74612000	-2.95031300	3.76064900
C	-4.04868200	1.66357400	0.49854300
C	-5.36191900	0.90384700	0.32315600
H	-4.07396900	2.53849400	-0.14930900
H	-3.94660200	2.02423800	1.52427300

C	-6.54535800	1.80018400	0.72277900
H	-5.48406600	0.60145100	-0.72034600
H	-5.38287000	-0.00477100	0.92498400
C	-7.89641500	1.10288300	0.54118300
H	-6.43145000	2.10919600	1.76844600
H	-6.52601800	2.72042500	0.12699900
H	-8.71886600	1.75997800	0.83325300
H	-8.05674700	0.81328000	-0.50148200
H	-7.96087800	0.19786900	1.15224500
C	-1.68032300	2.05349000	-0.06448700
C	-1.79331400	2.86518300	-1.35191400
H	-0.71787300	1.54149500	-0.05303600
H	-1.74002400	2.70861900	0.80738200
C	-0.73520500	3.98261100	-1.35166300
H	-1.62042200	2.22422100	-2.21848500
H	-2.78456800	3.31729600	-1.46585400
C	-0.76463800	4.81033000	-2.63869300
H	-0.89405100	4.63851200	-0.48752800
H	0.25563400	3.53497200	-1.22857400
H	-0.00578300	5.59569600	-2.61263100
H	-0.56416700	4.18464700	-3.51286900
H	-1.73742800	5.29119700	-2.78387800
Zn	1.75876200	-1.28842000	-0.41386900
Br	0.14034200	-2.79742600	0.49608200
Br	0.92045500	0.15931700	-2.16074700
N	-2.73629200	0.95267500	0.18390900
C	4.63960100	-2.68330800	-1.08945200

O	5.73709200	-2.56523200	-0.74103900
O	3.56533200	-2.87003100	-1.50408400

TS2

C	4.35992600	1.06559700	0.37766300
C	3.83610600	-0.14438800	1.15794000
H	5.31077900	0.85960900	-0.10911500
H	3.62498900	1.40199600	-0.34877400
H	2.98639600	0.18857800	1.76917700
Br	4.68804000	2.64649700	1.54756500
O	3.34804500	-1.07906100	0.20919000
C	4.87595800	-0.78850500	2.07186700
H	5.22481900	-0.07798600	2.82485400
H	4.43148900	-1.64661800	2.58081200
H	5.73298700	-1.13769800	1.49276500
C	-2.91174900	0.22864200	-1.02639100
C	-3.43409400	-1.20552700	-0.99216000
H	-1.88969500	0.21146400	-1.40904800
H	-3.51141600	0.84503200	-1.69781700
C	-3.45436800	-1.76818400	-2.42361200
H	-2.76740200	-1.82803900	-0.39153500
H	-4.43717900	-1.27112900	-0.56649300
C	-3.91063300	-3.22889000	-2.46674900
H	-4.11446100	-1.15655600	-3.05141200
H	-2.45075900	-1.68763600	-2.85364800
H	-3.91565500	-3.60544400	-3.49250000
H	-3.24041700	-3.86465000	-1.88227700

H	-4.92270700	-3.34447700	-2.06535200
C	-2.25222800	0.16954000	1.43912800
C	-3.19613600	-0.69812100	2.26890000
H	-1.77437800	0.89068800	2.10483300
H	-1.46807600	-0.44439200	0.99196300
C	-2.39687200	-1.40131900	3.38069700
H	-3.97993800	-0.09151800	2.73279100
H	-3.68617700	-1.45392300	1.65406000
C	-3.27763000	-2.30621700	4.24606400
H	-1.59315500	-1.98928800	2.92808500
H	-1.91393000	-0.64699500	4.01318300
H	-2.68785400	-2.78997800	5.02808600
H	-4.07808700	-1.74123100	4.73471800
H	-3.74143600	-3.09560200	3.64721000
C	-4.12781300	1.71155800	0.67806800
C	-5.44815400	0.96644500	0.49316300
H	-4.16652000	2.62225700	0.08259400
H	-3.99813200	2.01256500	1.71981800
C	-6.61723400	1.84352500	0.97065000
H	-5.59721200	0.72288100	-0.56221000
H	-5.45804300	0.02600500	1.04419100
C	-7.97566100	1.16137800	0.78650800
H	-6.47546300	2.09537200	2.02819200
H	-6.60874100	2.79436800	0.42485200
H	-8.78725300	1.80425500	1.13508600
H	-8.16415400	0.92950400	-0.26582300
H	-8.02857900	0.22474000	1.34900300

C	-1.77319800	2.13075100	0.08060200
C	-1.91709200	3.01687000	-1.15357600
H	-0.81200700	1.61762700	0.03635900
H	-1.81079500	2.73355200	0.99079300
C	-0.85987500	4.13472300	-1.11362100
H	-1.76453500	2.42878400	-2.06056000
H	-2.91068700	3.47350500	-1.21815800
C	-0.91986900	5.03518200	-2.34969700
H	-0.99970800	4.73927900	-0.20952800
H	0.13349700	3.68144800	-1.04027600
H	-0.16114500	5.81935600	-2.29654400
H	-0.73957100	4.46133600	-3.26288800
H	-1.89595100	5.52184000	-2.44428100
Zn	1.64097000	-1.37370700	-0.69236700
Br	-0.00737700	-2.78888900	0.29755400
Br	0.85082200	0.45300600	-2.05480100
N	-2.82541000	1.01823900	0.28936900
C	4.28046300	-2.06318000	-1.12343400
O	5.44182300	-1.98976800	-0.97078300
O	3.30687500	-2.45368200	-1.71502500

IV

C	-2.82574600	0.85462500	-0.43727000
H	-3.54710000	0.91902800	-1.25160000
H	-1.82519500	0.95203500	-0.85882800
C	-2.46779900	-1.45957900	-1.13790400
H	-2.88814000	-0.96189900	-2.01258200

H	-1.38178400	-1.36890300	-1.19745300
C	-1.87739500	-0.71352300	1.21781900
H	-0.97875400	-0.21313400	0.86031100
H	-2.29460100	-0.11810500	2.02938000
C	-4.27262100	-0.94702600	0.57889600
H	-4.41355500	-0.37636700	1.49732000
H	-4.24153800	-1.99986000	0.85420100
N	-2.88912400	-0.59692200	0.06744100
C	3.70999700	-1.72607400	0.32870600
C	3.52953700	-1.08306600	-1.04412900
H	4.13369000	-1.03040300	1.05006300
H	2.76848700	-2.12799000	0.69105800
H	3.16436800	-1.83105300	-1.74880600
Br	4.94345900	-3.27452800	0.26748000
O	2.49336500	-0.07665700	-0.88882200
C	1.17011900	-0.45689900	-1.03390000
O	0.39008000	0.54634700	-0.85348300
O	0.85295500	-1.61245100	-1.28024700
C	-3.08618700	1.95350600	0.58931600
C	-3.08730900	3.32766800	-0.10329900
H	-2.30999000	1.95572000	1.35818500
H	-4.04926400	1.80909500	1.09233400
C	-3.28798600	4.47852300	0.88594000
H	-2.13913100	3.46652300	-0.63367000
H	-3.87491600	3.35362300	-0.86621000
H	-3.28321200	5.44103400	0.36924900
H	-4.24203200	4.38811100	1.41538400

H	-2.48844100	4.49786500	1.63112000
C	-1.53150000	-2.10944200	1.72726800
C	-0.67150900	-1.99624200	2.99812600
H	-0.96788700	-2.65590100	0.96782500
H	-2.42916400	-2.69142500	1.96139300
C	-0.20571300	-3.36079300	3.51219500
H	0.19541600	-1.35949700	2.79506800
H	-1.24480600	-1.48474000	3.77995500
H	0.39850600	-3.25155800	4.41592900
H	-1.05456600	-4.00756900	3.75648600
H	0.40437700	-3.87879800	2.76642600
C	-2.88488100	-2.92969500	-1.15675900
C	-2.27937100	-3.61265000	-2.39590200
H	-3.97424700	-3.03344800	-1.19170800
H	-2.54224400	-3.45592600	-0.26510700
C	-2.65787500	-5.09272700	-2.49192000
H	-2.61515700	-3.08972100	-3.29929000
H	-1.19102300	-3.50494200	-2.36479400
H	-2.21704000	-5.55162800	-3.38014200
H	-2.30105700	-5.65062200	-1.62088100
H	-3.74268200	-5.22661000	-2.55289100
C	-5.43231700	-0.68583300	-0.38094800
C	-6.73925100	-1.27546800	0.17175100
H	-5.22882900	-1.12055100	-1.36399300
H	-5.56614300	0.38899900	-0.53219700
C	-7.94257800	-0.99343100	-0.73165900
H	-6.62351500	-2.35775800	0.30138000

H	-6.92845200	-0.86560100	1.17082000
H	-8.85538300	-1.42580700	-0.31524700
H	-8.10783300	0.08161100	-0.84885300
H	-7.79864500	-1.41898400	-1.72925000
Zn	1.28921700	2.18810900	-0.14578400
Br	1.77240000	3.90848500	-1.63082600
Br	1.03370600	2.11534800	2.20266000
C	4.75851800	-0.36811600	-1.57736400
H	5.08898200	0.40764100	-0.88167300
H	5.57501100	-1.07725400	-1.72227100
H	4.53008400	0.10382500	-2.53438700

TS3

C	2.57920200	0.21841200	-0.92989300
H	2.93755200	0.61891900	-1.87762700
H	1.57644800	-0.17931000	-1.08947900
C	1.33471200	2.31283200	-0.73216200
H	1.57147600	2.23341600	-1.79375700
H	0.37692300	1.81644000	-0.57394400
C	1.83207900	0.89916400	1.32187200
H	1.03878100	0.20280400	1.05251500
H	2.64924100	0.32149100	1.75199100
C	3.68014200	2.17014900	0.23069900
H	4.29451500	1.50841600	0.84175100
H	3.43539900	3.03824300	0.84019600
N	2.37487400	1.43534500	-0.01159000
C	-3.44756800	1.43765200	-0.43999900

C	-3.96696300	0.08107100	0.01673900
H	-3.43543100	2.26658700	0.24457800
H	-3.44275200	1.67132500	-1.49098900
H	-4.73793700	-0.27305100	-0.66003100
Br	-5.92175800	2.38763200	-0.73513000
O	-2.83962700	-0.87870700	-0.15992500
C	-1.67675500	-0.25703900	-0.26069000
O	-0.61205300	-0.91968600	-0.31271100
O	-1.71268300	1.01902400	-0.29646700
C	3.51688200	-0.87927000	-0.43351200
C	3.69042000	-1.95150100	-1.52399100
H	3.11556500	-1.35799600	0.46285700
H	4.50172500	-0.47361800	-0.17727500
C	4.58757700	-3.10510400	-1.06840400
H	2.70858200	-2.34593300	-1.80710900
H	4.10973600	-1.49108300	-2.42669300
H	4.69209700	-3.85105000	-1.85935100
H	5.59020700	-2.75164900	-0.80750200
H	4.16790600	-3.60692300	-0.19251700
C	1.32279100	1.90679700	2.34871400
C	1.05175400	1.19344100	3.68518200
H	0.39483900	2.36690300	2.00136500
H	2.04584100	2.71055100	2.52016400
C	0.46771600	2.13520100	4.74108400
H	0.37059900	0.35310300	3.51826800
H	1.98538100	0.75659300	4.05746300
H	0.28987600	1.60500900	5.67949800

H	1.14603000	2.96766100	4.95345700
H	-0.48692300	2.55733200	4.41374400
C	1.24479100	3.79235500	-0.35843000
C	0.12141800	4.45935500	-1.17241300
H	2.18529500	4.31023200	-0.56999000
H	1.03817900	3.92732000	0.70370300
C	-0.03149400	5.94807700	-0.85043400
H	0.32436200	4.33483400	-2.24262400
H	-0.82292900	3.94162500	-0.97769500
H	-0.83418800	6.39276200	-1.44255000
H	-0.27592200	6.10270900	0.20479500
H	0.88824800	6.50116400	-1.06604700
C	4.44814800	2.60055700	-1.01819900
C	5.63077400	3.50870000	-0.64558200
H	3.79291400	3.13556300	-1.71213800
H	4.82865500	1.72585900	-1.55334900
C	6.44999000	3.93566300	-1.86631500
H	5.25592100	4.39813600	-0.12629700
H	6.27967800	2.98709800	0.06739300
H	7.28048500	4.58221300	-1.57417100
H	6.86999800	3.06937700	-2.38575300
H	5.83518100	4.48826600	-2.58303200
Zn	-0.34243300	-2.90364000	0.00648000
Br	-0.60943000	-4.22985200	-1.85863000
Br	0.65943700	-3.01157400	2.11421300
C	-4.41488300	0.02375100	1.46384200
H	-5.28310200	0.67237600	1.58385600

H	-4.68904700	-0.99759600	1.73343700
H	-3.61874700	0.36181700	2.13397100
V			
C	2.72424200	1.81033600	1.77553000
H	3.20657300	2.65626600	1.28571000
H	3.23730900	1.64327100	2.72627400
C	4.58670700	0.48102600	0.91528500
H	4.96219900	1.50465300	0.93816600
H	4.84673500	0.02109700	1.87105100
C	2.42824400	-0.63744800	1.60400200
H	2.70027200	-0.53923200	2.65825600
H	1.34952500	-0.50791200	1.52406400
C	2.48769200	0.73978200	-0.49235900
H	1.40516500	0.69783100	-0.39547700
H	2.78677700	-0.14747700	-1.04509700
N	3.05959800	0.58521300	0.91685000
C	-6.04184400	0.24263300	0.51719300
C	-6.70398000	-0.67491000	-0.51833300
H	-6.03667900	-0.22217300	1.50696300
H	-7.15299300	-0.11556400	-1.34330600
H	-7.43012400	-1.36608400	-0.09439300
Br	-1.50991600	-0.89222800	1.90446900
O	-5.59692100	-1.44096700	-1.03763400
C	-4.45213400	-0.80451400	-0.73456700
O	-3.37562800	-1.15760800	-1.14796200
O	-4.66127800	0.24488300	0.05991900

C	1.24683900	2.10893100	2.00562500
C	1.09254300	3.42777300	2.78065900
H	0.76320200	1.30617400	2.56595900
H	0.70874500	2.18786500	1.05717500
C	-0.37537000	3.76392000	3.05976200
H	1.64222800	3.36733800	3.72890400
H	1.55211800	4.24430600	2.20984400
H	-0.46303300	4.70703200	3.60594100
H	-0.93947900	3.85374800	2.12820200
H	-0.85083300	2.98071600	3.65624900
C	2.81254400	-2.02169500	1.09304100
C	2.01487200	-3.09277500	1.85694400
H	3.88106500	-2.21190200	1.23517600
H	2.57945000	-2.11719000	0.02945300
C	2.34453000	-4.50735400	1.37491700
H	2.22427600	-3.00924600	2.93092400
H	0.94648000	-2.89933300	1.72991600
H	1.77265100	-5.25151500	1.93491300
H	2.09397400	-4.62445100	0.31715900
H	3.40756100	-4.74040000	1.50150200
C	5.26044500	-0.26261000	-0.23907300
C	6.77141900	-0.37789900	0.01894200
H	5.10170100	0.27434300	-1.17717500
H	4.84118900	-1.25950000	-0.37191100
C	7.51180200	-1.06128000	-1.13408500
H	7.19330900	0.62107800	0.18288400
H	6.94133100	-0.93849500	0.94570600

H	8.58182000	-1.13418100	-0.92500100
H	7.13503600	-2.07441300	-1.30134000
H	7.39205800	-0.50399800	-2.06775300
C	2.89083300	2.01636400	-1.22802300
C	2.52004800	1.91463600	-2.71645800
H	3.96544900	2.21358400	-1.13717300
H	2.36903600	2.87648700	-0.79812400
C	2.83367800	3.20063600	-3.48421800
H	3.05797800	1.07235500	-3.16700700
H	1.45446400	1.68411100	-2.80001800
H	2.56958600	3.09800700	-4.53958700
H	2.26652200	4.04631500	-3.08400400
H	3.89808000	3.45429100	-3.43063700
Zn	-1.38675500	-0.52502300	-0.50257300
Br	-1.24109000	1.81751100	-1.14879400
Br	0.09717400	-2.00929800	-1.69723100
C	-6.57019200	1.65798700	0.58184600
H	-7.61350200	1.64890000	0.91040500
H	-5.99171500	2.24803200	1.29398900
H	-6.51284400	2.13824800	-0.39745600